Defect-induced lateral chemical heterogeneity at Ni/GaN interfaces and its effect on the electronic properties of the interface

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Scanning photoemission microscopy (SPEM) has been used to investigate the effect of morphological defects in GaN films grown on a 6H–SiC substrate on the composition and electronic properties of Ni/GaN interfaces in the temperature range of 25–600 °C. The SPEM imaging and spectroscopy identified a direct relation between the defects and the development of spatial heterogeneity in the interfacial composition, best pronounced after moderate annealing at 300 °C. The Schottky barrier height measured at these heterogeneous interfaces changes with advancement of the Ni–GaN reaction at elevated temperatures but exhibits negligible spatial variations. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1404411]

The advancement of GaN technology imposes very stringent demands on the uniformity, thermal stability, and reproducibility of the contacts to GaN-based electronic devices. The premature degradation of the contacts is among the issues that have not been clarified yet.[1] Severe limitation of the performance of metal/GaN contacts can be caused by morphological and crystallographic defects of the GaN epilayers.[2] Such defects may change the electric properties of the interface not only by creating additional states in the GaN band gap but also by introducing lateral variations in the extent of the interfacial reactions. Because of its small lattice mismatch to AlN (1%) and GaN (3.5%), 6H–SiC is among the substrates mostly used in GaN epitaxy. Furthermore, its high thermal conductivity compared to the other substrate of choice, Al_2O_3, makes it the best substrate for high-power applications. On the other hand, the high cost and the deficiency in quality (e.g., the presence of micropipes and inclusions or scratches introduced during polishing and etching procedures) limits the use of SiC, because most of the defects may propagate into the growing GaN film.

In this letter, we present direct evidence of lateral chemical heterogeneity at the Ni/GaN interface, related to the presence of morphological defects in GaN grown on a 6H–SiC substrate. We used a scanning photoelectron microscope (SPEM) to study the temperature evolution of a very thin Ni film deposited on the GaN surface. Compared to the other spatially resolved techniques, such as transmission electron microscopy (TEM), secondary electron microscopy (SEM), atomic-force microscopy (AFM), and ballistic electron emission microscopy (BEEM), the advantage of SPEM is that simultaneously the interfacial chemical composition and its effect on band bending can be probed at submicrometer length scales.

The experiments were carried out with the SPEM at the ELETTRA synchrotron light source, where the x-ray microprobe was provided by a zone plate focusing optic.[3] The SPEM has two operation modes, imaging by collecting photoelectrons within a selected energy window while scanning the sample, and spectroscopy from a microspot. The use of 16-channel detector,[4] where each channel corresponds to a specific photoelectron kinetic energy, allows easy mapping of core-level shifts induced by band bending or interfacial reactions. The binding energy of the core-level peaks is referred to the equilibrium Fermi level, E_F, measured on the Ta clips holding the sample. The SPEM station has facilities for metal evaporation and specimen preparation and characterization with low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). During all procedures, the pressure in the chambers was kept in the low 10^{-10} mbar range. After SPEM measurements, the samples were also examined by SEM and x-ray fluorescence analysis (FA).

The Ni-Schottky contact was formed on ~ 1-μm-thick, unintentionally doped GaN layers ($n \sim 1\times 10^{17}\,\mathrm{cm}^{-3}$). The GaN films were grown by molecular-beam epitaxy (MBE) on n-$\mathrm{SiC}(0001)_{\mathrm{Si}}$ substrates (with an AlN nucleation layer), which favor Ga-face growth. The samples were annealed uniformly by direct resistive heating. The temperature was controlled using a pyrometer with accuracy ± 10 °C. An atomically clean GaN surface, confirmed by AES and photoemission spectra, was obtained by cycles of N_2 ion sputtering (0.6 kV) and annealing to 900 °C, a procedure adopted previously for GaN grown on sapphire or Si.[5–7] About 4 ML of Ni was deposited at room temperature (RT) through a 0.3 $\times 2$ mm^2 mask, which left a Ni-free GaN surface as a reference. 1 ML equals the GaN(0001) atomic surface density $\sim 1.14\times 10^{15}$ atoms/cm^2.

The sharpness of the patch edge was about 15 μm wide and allowed precise monitoring of the evolution of the interface in the Ni coverage range of 0–4 ML. The correction for surface photovoltage (SPV) effects, a natural result of the high photon flux density used in SPEM,[8] was made by measuring the shift of the Fermi edge, which appears in the Ni coverage range of 1–2 ML, with respect to the reference E_F. The equilibrium E_F position was reached at ~ 3 ML of Ni,

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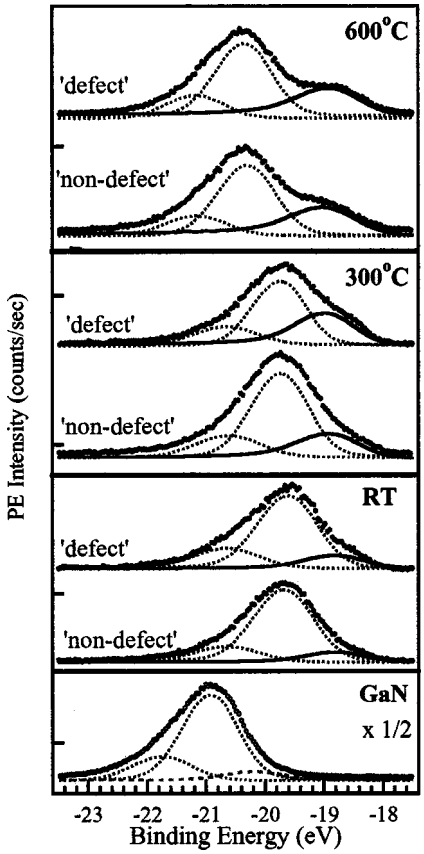

FIG. 1. Ga 3*d* spectra from GaN (bottom) and from defect and nondefect areas at the Ni/GaN interface measured before and after annealing at 300 and 600 °C. The GaN bulk components are drawn with dotted lines, the surface component with a dashed line, and the R–Ga component with a full line.

i.e., the Ga 3*d* and N 1*s* peaks of the GaN substrate inside the 4 ML Ni patch reflect only the band bending. By correcting for the SPV effect it has been established that the Schottky barrier height (SBH) has reached its final value already at Ni coverage of ~2 ML.

The Ga 3*d* semicore levels, shown in Fig. 1, are the most sensitive to the occurrence of a Ni–GaN interfacial reaction, which leads to degradation of the GaN top layers and release of Ga and N.[9] The Ga 3*d* spectra from GaN require two components, which account for the band dispersion of the Ga 3*d* semicore levels,[10] and one surface component, shifted by ~0.6 eV. All surface phases are in fact Ga adlayers, because Ga lowers the surface energy, eliminating the ionic contribution of the polar GaN(0001) surface.[11,12] Along with attenuation of the Ga 3*d* emission the Ni film leads to changes in the Ga 3*d* peak position, due to band bending, and replacement of the ''surface'' component by another component, R–Ga. Since the relative weight and the energy shift (0.9 eV) of the R–Ga are larger than that of the surface component in the GaN spectrum and increase after annealing, we assign the R–Ga as a product of the Ni–GaN interfacial reaction. The GaN N 1*s* peak at −398.8 eV underwent the same Ni-induced band-bending shift as the Ga 3*d* peak, accompanied by slight broadening at the high-binding-energy side. The evolution of the Ga 3*d* and N 1*s* spectra indicates the occurrence of a Ni–GaN interfacial reaction already at RT, leading most likely to formation of a dilute Ga solution in Ni.[13] The released N can recombine and desorb in the gas phase, can be trapped in the Ni–Ga interfacial layer, or can adsorb on top of the Ni film. Since no features related to adsorbed N atoms on Ni (a peak ~−397.0 eV) appeared in the N 1*s* region, we tentatively assign the N 1*s* peak broadening to N recaptured at the Ni–Ga layer. In support of this interpretation is our previous study of a Au/GaN interface, where a Au film with a similar thickness leads only to attenuation and band-bending shifts of the N 1*s* and Ga 3*d* spectra at RT.[7] Our data indicating a Ni–GaN reaction even at RT also are in agreement with the previous Auger and photoelectron spectroscopy analyses.[9,14] A discrepancy concerning the onset temperature of the Ni–GaN reaction and the formed reaction product exists in the investigations using thick Ni films and bulk probing techniques,[15,16] which apparently are less sensible to changes in the interfacial composition.

The Ga 3*d* and N 1*s* maps (not shown here) identified some sample regions with aligned darker areas. Figures 2(a) and 2(b) show Ga 3*d* and Ni 3*p* images of such a ''defect'' region measured after Ni deposition and following annealing to 300 °C for 120 s. The defect region is selected to be close to the edge of the Ni patch, so that direct comparison with the Ga 3*d* emission from the Ni-free GaN surface can be made. Spectroscopic examination was necessary to identify the origin of the observed contrast variations. The most peculiar spectroscopic finding is the C-rich spots in the defect areas, clearly manifested by the C 1*s* image and the spectra shown in Fig. 2(c). The C 1*s* peak, which is absent in the spectra from the uniform regions, has become the dominant feature in the C-rich spot. Since the Ga 3*d* and N 1*s* emission is strongly attenuated, these areas appear darker in the Ga 3*d* (N 1*s*) maps. Before annealing, the defects are not as well visible in the Ni 3*p* maps, a bit higher signal is seen in some defect spots. After annealing to 300 °C the Ni 3*p* maps clearly evidence enrichment of the defect areas with Ni. The chemical heterogeneity of the interface developed after annealing to 300 °C is best represented by the R–Ga map in Fig. 2(b) where the brighter areas indicate that a more vigorous interfacial reaction has occurred at the defects. This is confirmed by the more pronounced intensity of the R–Ga in the Ga 3*d* spectra from the defect areas (see Fig. 1, panel 300 °C). Further annealing to 600 °C led to strong attenua-

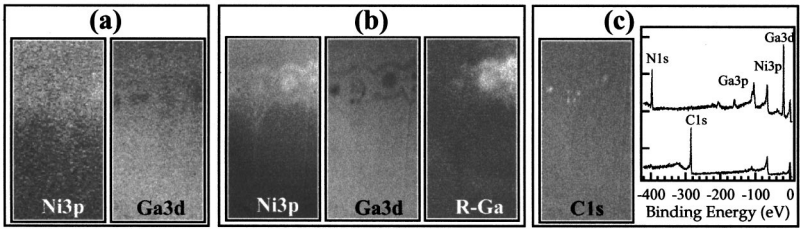

FIG. 2. Ni 3*p* and Ga 3*d* images ($25\times50\ \mu m^2$) taken at 25 °C (a) and after annealing to 300 °C (b). The R–Ga image in (b) manifests lateral variations in the interfacial reaction. (c) C 1*s* image and entire spectrum measured in the C-rich spots (bottom) and in the non-defect region (top).

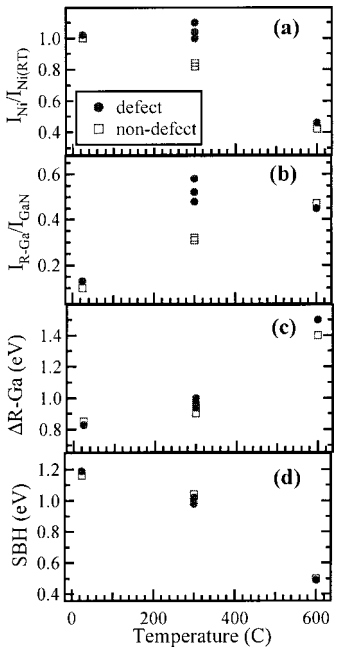

FIG. 3. Temperature-induced changes in the (a) normalized Ni intensity, $I_{Ni}/I_{Ni(RT)}$, (b) normalized R–Ga intensity, I_{R-Ga}/I_{GaN}, (c) energy shift of R–Ga, ΔR–Ga, and (d) SBH. Filled circles show the data from defect and open squares from nondefect areas.

tion of the Ni signal and homogenization of the interfacial composition as manifested by the Ga 3*d* spectra in Fig. 1 and the plots in Fig. 3(a)–3(c).

In order to clarify the origin of the defects SEM-FA analyses of the sample were performed after the SPEM experiment. The SEM micrographs revealed aligned holes at distances varying from submicron to more than 10 μm. The FA spectra taken in some holes showed an enhanced C emission and a weak Si signal. The latter should belong to the SiC substrate, because Si was not detected in the photoemission spectra. This can be explained assuming that the defects are micropipes (columnar voids) in the SiC substrate propagating in the GaN film. C is the most common contaminant that can be embed inside the holes and cannot be removed by our cleaning procedure.

Figure 3 shows four plots summarizing the temperature-induced changes in the composition and electronic structure of the nondefect and defect areas elucidated from the SPEM data. The normalized Ni 3*p* intensity, $I_{Ni}/I_{Ni(RT)}$ [Fig. 3(a)] evidences the aggregation of Ni at the defect areas and depletion of Ni from the surrounding nondefect surface, apparently facilitated by the increased surface mobility of Ni at 300 °C. The weight of the R–Ga component, expressed as I_{R-Ga}/I_{GaN} [Fig. 3(b)], represents the advancement of the interfacial reaction. The energy shift of the R–Ga component with respect to the GaN main component, ΔR–Ga [Fig. 3(c)], accounts for the chemical changes. After annealing at 600 °C the difference in the composition at the defect and nondefect becomes negligible, the Ni coverage decreases significantly, and the binding energy of R–Ga approaches the Ga 3*d* position of metallic Ga. This indicates penetration of a significant amount of Ni in the GaN lattice and replacement of the Ni-rich alloy film with a Ga-rich film.

The temperature-induced changes in the interfacial composition naturally affect the SBH, as illustrated in Fig. 3(d). The SBH increase measured at RT (1.18–1.2 eV) is within the values reported in the literature of 0.98–1.2 eV,[1,17] assuming flatbands for the clean GaN surface. The plots in Fig. 3(d) manifest a clear trend of lowering of the SBH after annealing, i.e., with increasing Ga and decreasing Ni concentration in the interfacial film. A simple phenomenological interpretation of this SBH lowering can be related to the trend towards the smaller work function of Ga,[17,18] however, keeping in mind the present case of a reactive interface.

The most peculiar finding here is the very small SBH lateral variations despite the chemical heterogeneity of the interfacial layer, best manifested by the composition difference between the defect and nondefect areas developed after annealing to 300 °C. This result can be explained assuming that the stoichiometry of the interfacial Ni–Ga layer is controlled by the reaction temperature leading to very similar Ni–Ga alloy composition. Indeed, the plots in Figs. 3(a) and 3(b) show that the weight of the R–Ga component after annealing to 300 °C varies in concert with local Ni coverage. Another possible explanation is a lateral surface change transport between the defect and nondefect areas resulting in leveling off of the SBH differences.

In conclusion, the present SPEM study of a Ni/GaN interface has revealed that defects in the SiC substrate propagated into the GaN epilayers may act as active trapping centers of the metal, resulting in formation of a laterally heterogeneous interface. Such lateral variation in the composition and local electron density can severely affect the local conductivity and degrade the contacts in GaN-based devices.

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